A STUDY OF
BUTADIENE POLYMERS AND COPOLYMERS

BY

HERBERT FINEBERG

B.S., Trinity College, 1935

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS
1941

A STUDY OF
BUTADIENE POLYMERS AND COPOLYMERS

BY
HERBERT FINEBERG
B.S., Trinity College, 1935

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1941

URBANA, ILLINOIS
1941

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. C. S. Marvel for his invaluable assistance and encouragement.

The author also is grateful to the University of Illinois and, in particular, the College of Chemistry.

A STUDY OF BUTADIENE POLYMERS AND COPOLYMERS

Introduction

Heating[2,1] liquid butadiene is known to cause both polymerization and dimerization. The structure of the thermopolymer has been established by Pummerer.[3] The sodium-catalyzed[1] and emulsion[4] reactions of butadiene lead only to polymers.

Investigations of the thermo dimer[2] have disclosed that it is a mixture of C_8 H_{12} isomers, the structures of which are not definitely known. The thermo dimer is reported[2] not to polymerize or to form a heteropolymer with sulfur dioxide.[5]

Glavis[6] has reported that alkaline degradation of olefine and cyclohexene polysulfones leads to the following products:

a. Olefine polysulfones $\rightarrow$ $RCHO + RCHCH_2CO_2CH_3$ (with SO_2Na on the second R)

b. Cyclohexene polysulfone $\rightarrow$ $\Delta^?$-octahydrobiphenyl + sodium Δ^1-cyclohexenesulfinate (1)

Both types of poly sulfones are of the "head to head," "tail to tail" type.

Discussion of Results

Sodium at 25-40°, resorcinol at 150°, and boron trifluoride at -70° have been found to convert butadiene to polymers without formation of dimers. Butadiene and ethyl α-chloracrylate, or α- chloracrylic acid, with ascaridole produce only copolymers. Of these polymers and co-polymers only the sodium-catalyzed polymer is soluble. A chloroform solution of the latter is ozonized and yields formaldehyde, indicating the presence of vinyl groups in the polymer. Hydroquinone, catechol, benzidine, bromine and iodine in <1.5 per cent quantities cause dimerization as well as polymerization. Hydroquinone gives the best yield of dimer (95 per cent).

The structure of the hydroquinone-catalyzed dimer has

been determined. Reduction gives ethylcyclohexane. The dimer adds bromine to yield a mixture of tetrabromides, m. p. 68-70°. Oxidation with nitric acid produces β- carboxyadipic acid, and the secondary oxidation products, oxalic and succinic acids. β- Carboxyadipic acid has been synthesized for comparison.[7] The formation of the latter establishes the presence of 1-vinylcyclohexene-4. The failure to find any other oxidation or reduction products, and the constant boiling point and refractive index of the dimer, indicate the absence of any isomers in the latter.

The dimer adds nitrosyl chloride and forms an oil. Aluminum chloride, p-tosylic acid, benzoyl peroxide and sodium do not cause the dimer to polymerize. Liquid butadiene, dimer and 1 per cent sodium at 25-30° produce polybutadiene and unreacted dimer, indicating that the dimer is not an intermediate in the sodium-catalyzed polymerization of butadiene. Boron trifluoride and dimer at -70° react slowly and the reaction product is unstable at 25°. The dimer does not copolymerize with vinyl chloride, ethyl α- chloracrylate, or α-chloracrylic acid. With liquid sulfur dioxide the dimer gives a polysulfone.

The polysulfone has been degraded with alkali to give an unidentified diketo compound and a di (chloromercuri) sulfone, the latter derived from a sulfone disulfinic acid. The latter is also isolated as a sulfinamide. These degradation products are the ones to be expected from the polysulfone of a hydrocarbon which is both an olefine and a cyclohexene, such as 1-vinylcyclohexene-4. The structure of the dimer polysulfone is postulated as a cross-linked "head to head," "tail to tail" type.

Bibliography

1. Harries, Ann., **383** (1911).
2. Lebedev and Skavronskaya, J. Russ. Phys.-Chem Soc., **43**, 1124 (1911); Lebedev, J. Gen. Chem. U.S.S.R., **5**, 1839 (1935).
3. Pummerer, Rubber Chem. Tech., **8**, 39 (1935).
4. Hill, Lewis, Simonsen, Trans Faraday Soc., **35**, 1067 (1939).
5. Kranze, Trudy Gosudarst Opyt. Zavoda Sintet. Kauchuka., Litera B. IV. ibid, Chem Abstracts, **31**, 7036 (1937).
6. Glavis, Ph.D. Thesis, University of Illinois, 1938.
7. Haworth and King, J. Chem Soc., **105**, 1350 (1919).

VITA

The writer was born in Portland, Maine, on January 16, 1915. He attended grammar school and two years of high school in that city, but was graduated from Weaver High School in Hartford, Connecticut, in June, 1931. In September, 1931, he matriculated at Trinity College, Hartford, Connecticut, from which institution he was graduated with the degree of Bachelor of Science in June, 1935. From June, 1935, to September, 1938, he was employed as research chemist by the Eastman Kodak Company of Rochester, New York. In September, 1938, he entered the Graduate School of the University of Illinois and held an appointment as an assistant in chemistry from September, 1939, to July, 1941 at that institution, while studying for the degree of Doctor of Philosophy.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0004